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Synthesis and Study of Polypyrrole Thin Films by Silar Method

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ABSTRACT

Polypyrrole (PPy) thin films were deposited by simple Successive Ionic Layer Adsorption and Reaction (SILAR) method on glass and stainless steel substrate from aqueous solution. The structural, optical and electrical properties were studied by means of X-ray Diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy, Raman Spectroscopy and UV–VIS spectrophotometer. The surface morphology and wettability properties were studied by means of Scanning Electron Microscope (SEM) and Contact angle meter. Electrical resistivity measurements by four point probe method.

Keywords: Polypyrrole, SILAR, FTIR, SEM, XRD, Raman Spectrum.

1. INTRODUCTION

Conjugated conducting polymers such as Polypyrrole (PPy), Polyaniline (PANI), Polythiophene (PT) and so forth are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. They are easy to prepare in the form of large area thin films and are capable of storing charge throughout their entire volume[1,2] in this PPy and PANI can be formed chemically or electro-chemically through oxidative polymerization of Pyrrole and aniline monomers. The Polypyrrole (PPy) is advantage of low oxidation potential of Pyrrole. Polypyrrole (PPy) based polymer blends can protect the corrosion of metals[3], because of the strong adhesion of PPy to iron or steel treated with nitric acid, PPy polymers can be used as

good adhesives[4]. The typical polypyrrole which is insoluble and infusible, exhibits poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole by both electrochemical and chemical routes. Among them, a significant strategy approach both high electrical conductivity and desirable mechanical properties of polypyrrole and other polymers[5-7]. A variety of applications towards technology of these conducting polymer materials has been proposed and demonstrated, viz. Rechargeable batteries, Electrochromic displays and Smart windows, Light Emitting Diodes (LEDs), Toxic waste cleanup, Sensors, Corrosion inhibitors, Field Effect Transistors (FETs), electromagnetic interference (EMI) shielding etc[8]. So preparation of PPy thin film in chemical and electro chemical preparation method is more effort have been taken. Here we choose the simple, less expansive SILAR method for synthesis of PPy thin film. The PPy thin films were deposited on the different substrate. After deposition, films were rinsed with distilled water to remove the monomer free. In the present investigations attempts were made to report on our observation of structure morphology, optical and electrical properties of polypyrrole thin films using the SILAR technique.

2. EXPERIMENTAL

2.1 Materials

The Pyrrole was obtained from Sigma-Aldrich (C_4H_5N, M.W. 67.09) reagent grade was distilled prior to use. Analytical grade of ammonium per-sulphate APS ($(NH_4)_2S_2O_8$ M=228.20g/mol) Merck Specialities Mumbai and used as received without any further purification. H_2SO_4 were obtained from Nice Chemicals Kochi.

2.2. Preparation of Polypyrrole Thin Film

Polypyrrole (PPy) thin films were deposited by simple successive ionic layer adsorption and reaction (SILAR) method on glass and stainless steel substrate from aqueous solution. The growth of Polypyrrole thin films was carried out by the SILAR method at room temperature. The SILAR method consists of two (or more than two) chemical baths. Polypyrrole film was prepared from the oxidation of 0.1 M solution of Pyrrole dissolved in 50 ml of 0.1 M H_2SO_4 (First chemical bath) and 0.1 M Ammonium per sulphate (APS) dissolved in 50 ml of 0.1M H_2SO_4 (Second chemical bath). The 0.1M ammonium per sulphate in 50 ml of 0.1 M H_2SO_4solution was used as a cationic and 0.1M Pyrrole in 50 ml of 0.1 M H_2SO_4 solution was used as an anionic precursors. One SILAR cycle consists of two steps: (1) adsorption of Pyrrole cations for 10s, (2) reaction with ammonium per sulphate precursor solution for 10s to form stable Polypyrrole. The higher concentration of precursor solutions resulted in to a higher growth rate but the quality of the film was poor due to powdery deposit. In order to prepare monomer free deposited film, after complete deposition, the deposited films were rinsed with double distilled water.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

The FTIR spectrum of the polypyrrole thin film is shown in Figure 1.

The spectrum in the range of 400 to 4000 cm-1 shows the presence of expected peaks of the polypyrrole.

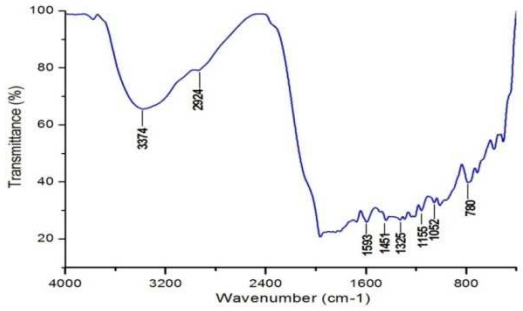

Figure 1 FTIR spectrum of polypyrrole thin film

The peak observed at 3374 cm^{-1} has been assigned for N-H stretching of nitrogen in the Pyrrole rings. The peak observed at 1593 cm^{-1} assigned for conjugated double bands C=C stretching vibration[9]. The peak 1325 cm^{-1} due to C-H bending vibrations and peak 1451 cm^{-1} assigned to typical polypyrrole ring vibrations. The small peak 1325 cm^{-1}, 1052 cm^{-1} may correspond to =C-H band in plane vibration. The small peak 1155 cm^{-1} assigned for N-C stretching band [10]. The peaks observed in the present work match well with literature so confirming the formation of polypyrrole structure of thin films in SILAR method.

3.2 FT-Raman Spectroscopy Analysis

Raman spectroscopic study is one of the important tools to obtain structural information on polymers. In most cases, Raman scattering is sensitive to the degree of crystallinity in a sample. Typically, a crystalline material yields a spectrum with very sharp and intense Raman peaks, while an amorphous material shows broader and less intense Raman peaks.

The Raman spectra of PPy thin film shows **Figure 2**, The most important peak at about 1588 cm^{-1} which can be attributed to the C=C backbone stretching of PPy[11]. The peak at about 1037 cm^{-1} is assigned to the C-H in plane deformation. Another peak at 1392 cm^{-1} is attributed to the ring-stretching mode of PPy. The band located at about 924 and 980 cm^{-1} are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively[12-14].

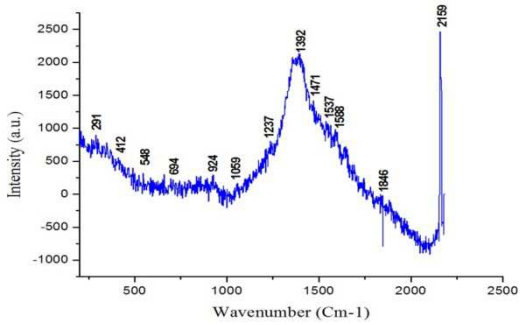

Figure 2 Raman spectrum of polypyrrole thin film

3.3 X-Ray Diffraction Analysis

The X-ray diffraction (XRD) studies of the samples were done on Rigaku X-ray Diffractometer with Cu – Kα radiation operating at 40kV and 15 mA. Scanning was carried out in the 2θ range from **10** to **90^0** at a scan speed of **10^0** per minute. A typical X-ray diffraction pattern for polypyrrole thin film prepared by SILAR method is shown in Figure 3. PPy thin film which can clearly indicated that they are amorphous nature. The broad peak observed at about **$2\theta = 23.8^0$** which is characteristic conducting amorphous polypyrrole[15-17]. The crystallite

size from a sharp peak at **23.8^0** for PPy is estimated by using scherrer's formula leads to the crystallite size of about **85.003 nm** for PPy thin films. The d- spacing value of PPy thin film is **3.7342 Å.**

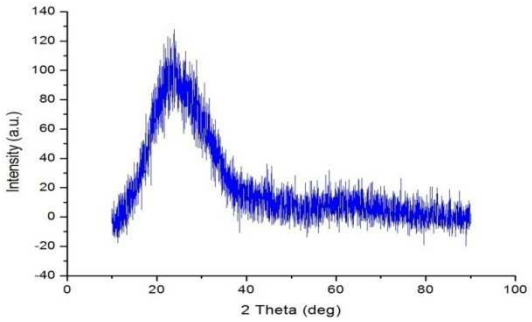

Figure 3 X- Ray diffraction pattern of polypyrrole thin film

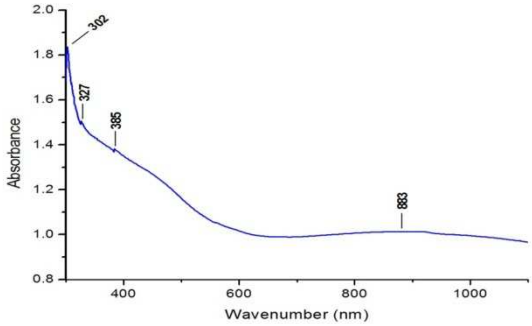

Figure 4 UV-Vis absorbance spectrum of PPy Thin film

3.4. UV – Vis Spectroscopy Analysis

The UV- Vis spectroscopy of polypyrrole thin film is shown in the **Figure 4**. These absorption spectra have been recorded over wavelength range 300 to 1100 nm using a Lambda 35 UV-Vis spectroscopy model at room temperature. The absorption peak 302 nm attributed π - π^* inter band transition. The absorption peak at 327 nm is attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to π - π^* electron transition[18-21]. We also observed two absorption peaks at about 385 nm and 883 nm this peak assigned to the polaron and bipolaron band transitions for Polypyrrole[22-26].

3.5 Scanning Electron Microscopy Analysis

The SEM study of PPy films shows **Figure 5** demonstrated that the surface was covered with grains. The scanning electron microscopy shows the particles have irregular rice-grain morphology. The particles nearly spherical and rod types are present in glass substrate.

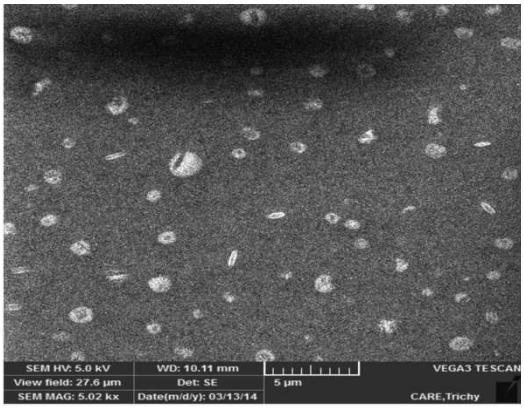

Figure 5 Typical SEM image of PPy Thin film

3.6 Surface Wettability study

The surface wettability properties are studied by means of contact angle meter. Thicknesses of polypyrrole thin films were calculated by maximum thickness of 2641A^o

at 20 deposition cycles. As the number of deposition cycles increases the value of contact angle decrease so this result confirmed that the polypyrrole thin film as a hydrophilic nature[27].

3.7 Conductivity study

Thin films of PPy sample were measured for resistance using four-point probe technique. The four probe technique is a very efficient method for measuring the sheet resistance[28,29]. It measures the sample resistance by current that flows for a given applied voltage. The outer two pins force a current through the sample and the inner two pins measure the voltage drop. The resistance of the pure PPy Thin films variation of electrical resistance as a function of temperature[30]. In this case it was observed that as temperature increases the electrical resistance decreases and hence conductivity increases so in this thin films thermally activated behaviour nature of conductivity has been confirmed.

4. CONCLUSIONS

The thin film of PPy was successfully synthesized by SILAR method. The structure of PPy confirmed by FTIR, XRD and Raman Spectroscopy techniques. UV-Vis studies showed that the formation polaron and bipolaron states of PPy thin films. The pure PPy thin film shows a thermally activated of conductivity confirmed by four-point probe method. The surface wettability study confirmed by number of SILAR cycle increases the thin film contact angle decreases and also thin film insoluble hydrophilic nature.

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